

Atoms in carbon cages: the structure and properties of endohedral fullerenes

D. S. Bethune, R. D. Johnson, J. R. Salem, M. S. de Vries & C. S. Yannoni

Encapsulating atoms or molecules inside fullerene cages could give rise to a myriad of novel molecules and materials. The existence of such species is now strongly supported by a growing body of experimental evidence. Fullerene-metal complexes generally thought to be endohedral are being produced and purified in milligram quantities, and their structure and properties are beginning to be explored.

THE notion that atoms could be trapped in fullerene cages¹ was soon supported by mass spectral evidence that lanthanum-fullerene complexes were produced by laser vaporization of lanthanum-impregnated graphite (see Fig. 1)². Some early studies disputed this idea^{3,4}, but subsequent experiments have provided further support. Until mid-1991 endohedral fullerenes were produced only in minute quantities and few experiments were reported. This situation changed dramatically in 1991 when techniques to produce metallofullerenes in bulk (by laser⁵ or arc-vaporization^{5,6} of graphite-metal composites in helium) were developed, allowing the first detailed spectroscopic characterization of a metallofullerene⁶ and leading to numerous experimental studies of endohedral fullerenes. Theoretical methods to calculate the structure of these complex entities are also being developed.

What properties might endohedral fullerenes be expected to have? By analogy with alkali-doped fullerenes, in which electrons are donated to the fullerene cage by interstitial metal atoms⁷, the conductivity of solid metallofullerenes will depend on the internal dopant; some may be superconductors⁸. Caged lanthanide ions will have optical transitions involving unfilled *f*-shell orbitals which would be determined by the crystal field due to surrounding carbon atoms. The resulting energy levels could provide a basis for a metallofullerene laser. Encapsulation of refractory metals such as uranium may allow such species to be conveniently put into solution, or volatilized without resorting to fluorination. It has been proposed that endohedral fullerenes containing small polar molecules could be assembled into useful ferroelectric materials^{9,10}. Experimental progress has been hindered by difficulties in separating the endohedral complexes from other fullerene species: however, samples of pure metallofullerenes have recently been obtained and these suggestions may soon be put to the test. The production of fullerenes containing internal species complements the extensive recent work on fullerene chemistry involving reagents outside the carbon cage¹¹.

Here we review existing methods for producing metallofullerenes and describe the work that has been done to characterize their structure and physical properties. The latter has relied to a large extent on techniques that probe electronic structure, and has focused on the nature of charge transfer between the metal and the fullerene cage. We then discuss theoretical studies of these compounds and how these compare with experiment, and finally we consider the future prospects for detailed structural characterization and possible applications.

Production techniques

Metallofullerenes can be produced by simply adding metal to carbon vapour in a standard fullerene generator¹². Chai *et al.* produced the first macroscopic amounts of metallofullerenes by laser vaporization of a graphite-metal composite rod in a helium-filled tube-oven at high temperature⁵. Mass spectra of material sublimed from the recovered soot showed normal fuller-

enes, and peaks corresponding to La@C_{2n} with 2n = 60, 70, 74 and 82; the '@' notation denotes an endohedral complex⁵. (Despite the present lack of direct structural evidence, we will use the '@' sign to designate species that we presume have endohedral structures.) Only La@C₈₂ was detected by mass spectrometry in toluene solutions of the sublimate. Subsequently the laser vaporization technique was used to produce Y@C_{2n} and Y₂@C₈₂ species¹³, a large number of U_n@C_{2n} species including U@C₂₈ and U₂@C₆₀ (ref. 14), and a M@C₆₀ species, Ca@C₆₀ (refs 15, 16).

Most recent metallofullerene production has used the arc or resistive heating methods. Chai *et al.* reported production of detectable amounts of La@C₈₂ by arc-burning carbon electrodes packed with La₂O₃, graphite powder and pitch⁵. Following this lead, our group at IBM arc-vaporized a rod made by pressing and baking a graphite-La₂O₃-dextrin mixture⁶. We subsequently simplified this technique by using cored carbon electrodes packed with dry mixtures of metal (or metal-oxide) and graphite powders¹⁷⁻¹⁹. The arc-vaporization technique produces soots that contain numerous metallofullerenes. A relatively small subset of these are sufficiently stable and soluble to allow extraction from the soot with solvents such as toluene, pyridine and carbon disulphide (CS₂). This subset includes M@C₈₂ species (with M = Sc, Y and La^{6,18-28}), di-metal species including La₂@C_{80,82} (refs 20, 22) and Y₂@C_{80,82} (refs 18, 19, 22, 25), di- and tri-scandium metallofullerenes^{17-19,24,29}, and many other mono- and di-metal rare-earth metallofullerenes^{19,30}. A recently introduced method for producing fullerenes is plasma-torch vaporization of carbon black and, for metallofullerenes, metal oxide³¹. Yields of Y@C₈₂, Y₂@C_{82,84} and normal fullerenes comparable to those obtained with arc techniques have been achieved³¹. Another unusual method—operating a carbon arc in a He-Fe(CO)₅ atmosphere—reportedly produced bulk quantities of a FeC₆₀ complex^{32,33}. Recently a CoC₆₀ complex was detected in soot, but could not be extracted³⁴.

Production of metallofullerenes has generally been inefficient. Typically they constitute less than a few weight per cent of the extractable species (or $\leq 10^{-3}$ of the soot). Yields are limited in part by the reactivity and scant solubility of metallofullerenes. They have solubilities similar to higher fullerenes, dissolving better in pyridine and CS₂ than in toluene^{22,25}. Production efficiency improves if metal carbides are used as metal sources, or if the carbide-rich cathode deposit produced *in situ* during arc-vaporization of a metal-containing bar is 'back-burned' by reversing the arc polarity²⁶. The fraction of metallofullerenes (especially multiple-metal fullerenes) increases with increasing metal loading, although overall fullerene yield falls³⁰. Anaerobic preparation increases the yield of some metallofullerene species^{23,27,29}.

An increasing variety of species have been successfully encapsulated in fullerenes. Significant quantities of fullerenes containing rare-gas atoms have been produced and detected³⁵, and

results suggesting that CO (ref. 36) and CN (ref. 37) have been trapped in fullerenes have been reported. Large metallofullerenes, containing up to 3 or 4 lanthanum atoms in cages made from >100 carbon atoms, have been found^{38,39}. Much larger fullerene-related structures, including concentric multi-walled graphitic tubules⁴⁰⁻⁴³ and polyhedra^{43,44}, and single-walled nanotubes^{34,45,46}, have been made recently. Partial filling of the multi-walled tubules⁴⁷⁻⁴⁹ and polyhedra⁵⁰⁻⁵³ with metal carbides or metals has been reported. Recently, electron beams (in a transmission electron microscope) were used to pierce holes in these gigantic endohedral fullerenes⁵³ and to drive an initially encapsulated gold nanocrystal out through the wall of a graphitic polyhedron⁵². Filled tubules could conceivably serve as nanometre-scale wires, whereas encapsulated single-domain ferromagnetic nanocrystals might have applications in data storage or in ferrofluids. Production techniques essentially identical to those used for metallofullerenes have now created mixed-atom cages dubbed metallocarbohedrenes⁵⁴⁻⁵⁹.

Characterization

Characterization of samples containing the presumed endohedral complexes has the aim of finding which species are produced, assessing their relative abundance, stability, and chemical reactivity, and determining their structure. Numerous techniques have been brought to bear.

Mass spectrometry. Molecular-beam techniques and mass spectrometry have provided very powerful tools for fullerene

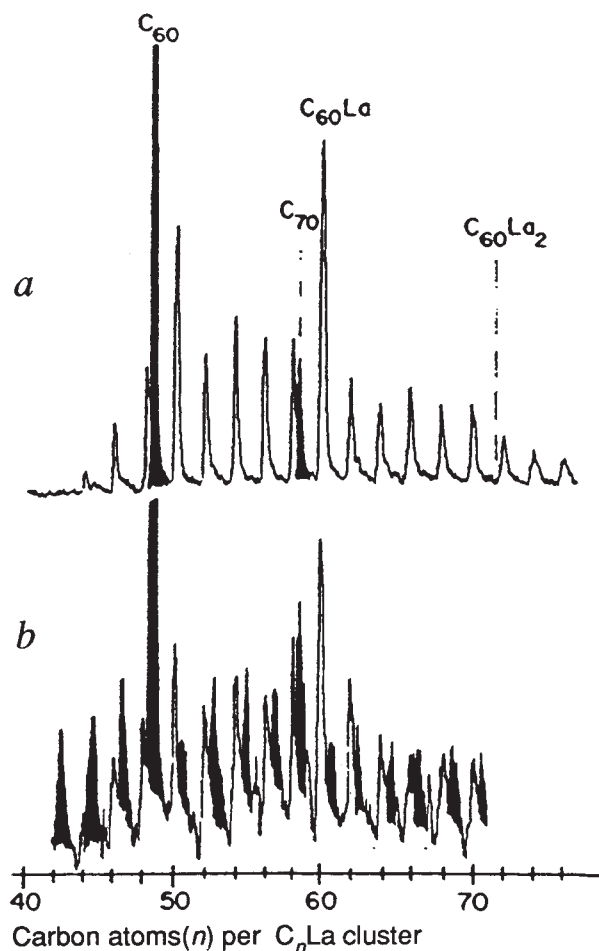


FIG. 1 Mass spectrum of $\text{La}@C_{2n}$ complexes and empty C_{2n} molecules (darkened peaks) produced by laser vaporization of a lanthanum-impregnated graphite disk. ArF ionization laser fluence in (a) was $1-2 \text{ mJ cm}^{-2}$, and in (b) was $<0.01 \text{ mJ cm}^{-2}$. (From ref. 2, with permission.)

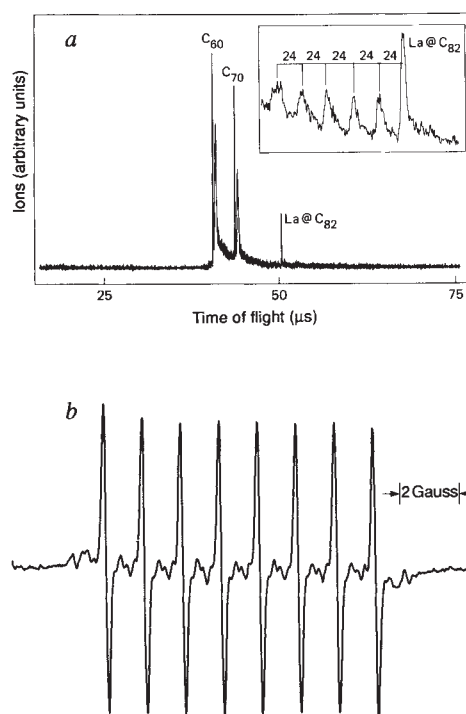


FIG. 2 a, Mass spectrum of the toluene extract of soot produced by arc-burning a La_2O_3 -graphite composite bar. Laser-desorption/laser ionization (wavelengths 248 nm and 193 nm respectively) time-of-flight mass spectrometry was used. The inset shows the fragmentation behaviour at high incident powers of ionization-laser radiation. b, EPR spectrum (9.5112 GHz) at ambient temperature of a degassed toluene solution of the same extract in 1,1,2,2-tetrachloroethane. (From ref. 6, with permission.)

research^{60,61}. This combination of techniques provided the crucial evidence^{1,62} that led to the discovery of fullerenes and endohedral fullerenes². The mass spectrum of our first lanthanum-fullerene sample is shown in Fig. 2a (ref. 6). The La-fullerene soot was inadvertently spiked with ^{13}C -enriched normal fullerene soot before toluene extraction. The spectrum is dominated by three mass peaks corresponding to C_{60} , C_{70} and $\text{La}C_{82}$. The absence of ^{13}C -enriched satellites to the $\text{La}C_{82}$ peak confirms that this metallofullerene was not generated in the laser-desorption or ionization steps in the mass spectrometer but was present in the extract.

The inset in Fig. 2a shows that increasing the power of the incident (ionization) laser radiation causes the $\text{La}@C_{82}$ to fragment by shedding C_2 units, rather than by losing the metal atom, as originally reported by Weiss *et al.*⁶³. That observation, and the abrupt termination of the sequence of daughter-metallofullerene fragments at $\text{La}@C_{44}$, gave rise to the 'shrink-wrap' notion: the cage can lose carbon dimers and shrink about a trapped atom until, at a minimum size dependent on the trapped species, it bursts⁶³. An additional demonstration of how tightly the metals in metallofullerenes are bound was provided by Yeretizian *et al.*, who collided $\text{La}_2@C_{80}$ ions with a surface using a modified time-of-flight apparatus. No metal dissociation occurred even at 200-eV incident energy⁶⁴. Inert-gas/fullerene complexes made by gas-phase ion-molecule reactions, when subjected to secondary gas-phase collisions, show a similar reluctance to part even with helium⁶⁵⁻⁷⁴. Here again C_2 units are lost preferentially, clearly implying that the inert gas atom must be inside the cage.

Ion cyclotron resonance mass spectrometry was used by Weiss *et al.* to show that the metals in metallofullerene ions are shielded from chemical attack⁶³. Recently, gas-phase association

reactions in Fourier-transform-ICR machines have been used to create and trap exohedral metal–fullerene complexes^{75–78}. This technique allowed McElvany to compare directly the reactivity of N₂O with exohedral YC₆₀ to its reactivity with YC₆₀ complexes formed by a laser vaporization method. The exohedral complex reacted readily to give YO, whereas the directly produced complex showed essentially no reaction, despite exposure to a higher ($\times 10^3$) concentration of N₂O (ref. 78). This experiment confirms the early results of Weiss *et al.*⁵³ and provides compelling additional evidence for the endohedral nature of the laser-produced complex.

The properties of metallofullerenes exacerbate some difficulties in using mass spectrometry for fullerene characterization. It is found that the mass spectrum obtained depends drastically on how the sample molecules are put into the gas phase^{19,79}. Metallofullerene soot, analysed by laser-desorption mass spectrometry, contains a wide variety of metallofullerenes; their relative abundances are similar to the corresponding bare fullerenes (M@C₆₀ is typically the most prominent). But only a few metallofullerenes survive vacuum sublimation, notably M@C₈₂, and to some extent, M@C₇₄ and M@C₈₀ (ref. 19). A recent study⁷⁹ comparing laser- and thermal-desorption mass spectra of metallofullerene raw soots concluded that trivalent elements preferentially form endohedral complexes involving 60, 74 and 82 carbons, and that these species can survive slow thermal desorption. In contrast, divalent metals, such as Ca, Sr, Sm, Eu and Yb, preferentially form M@C₆₀ species that do not survive thermal desorption.

A difficulty that arises if photoionization is used is that the ionization cross-sections may vary, so ion peak heights may not indicate relative abundances correctly. This effect is notably exaggerated when normal and metallofullerenes are compared using 193-nm laser ionization, because ionization of the former requires two such photons, whereas metallofullerenes sometimes require only one, and are therefore detected with much higher efficiency^{4,19}.

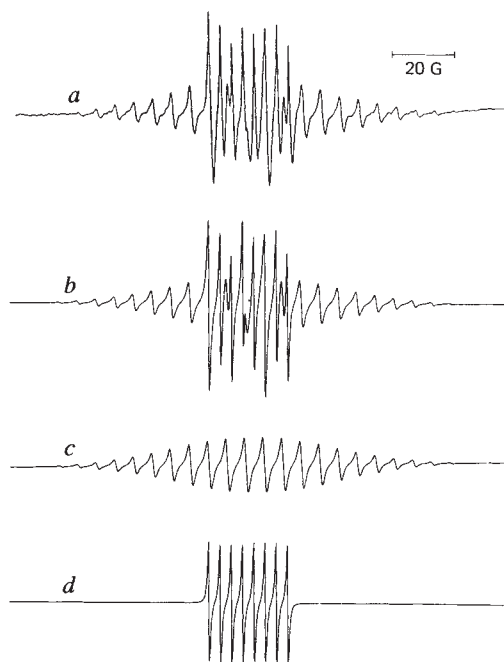


FIG. 3 The EPR spectrum of a toluene solution of toluene extract from soot produced by arc-vaporization of a carbon electrode with a scandium-packed core. (a) Experimental spectrum, (b) superposition of two simulated spectra arising from an unpaired electron spin coupled to (c) three equivalent scandium nuclei and (d) a single scandium nucleus. (From ref. 17, with permission.)

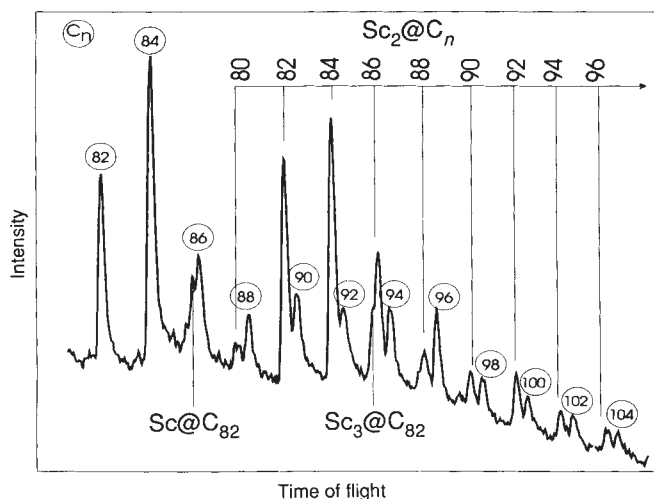


FIG. 4 Mass spectrum of the scandium metallofullerene sample. The dominance of Sc₂@C_{82,84,86} species is evident.

Electron paramagnetic resonance. EPR spectroscopy has yielded detailed information about the electronic structure and chemical nature of several metallofullerenes, even though they constituted at most 2% (and often much less) of the fullerene extracts. The first metallofullerene EPR spectrum, EPR of La@C₈₂ in solution, is shown in Fig. 2b (ref. 6). The observation of eight equally-spaced lines provides dramatic and unequivocal confirmation of isotropic electron–nuclear hyperfine coupling (h.f.c.) to ¹³⁹La with nuclear spin quantum number 7/2 (ref. 80); the electron g-value of 2.0010, close to that measured for the C₆₀ radical anion^{81–84}, indicates that a single unpaired electron (doublet state) resides in the lowest unoccupied molecular orbital (LUMO) of the fullerene cage. Each ¹³⁹La hyperfine line shows ¹³C hyperfine satellites, proving that the unpaired electron couples to both the ¹³⁹La and the fullerene-cage carbon atoms. The 1.2-G ¹³⁹La h.f.c. is very small compared to 50-G h.f.c. measured for La²⁺ substituted in CaF₂ (ref. 80) and –196-G h.f.c. calculated for La²⁺ using unrestricted Hartree-Fock (UHF) wavefunctions. Therefore, it was concluded⁶ that the lanthanum atom must be in its preferred 3+ oxidation state, and that the structure is most appropriately written La³⁺@C₈₂^{3•–}. Subsequent theoretical calculations^{85,86} and EPR studies^{23,28} have strongly supported this conclusion. Recent results on purified La@C₈₂ (ref. 28) confirm that the EPR spectra were correctly assigned.

EPR spectra obtained for Y@C₈₂ showed that the yttrium in this species is also in the 3+ oxidation state^{13,18,25}. A Y₂@C₈₂ species observed by mass spectrometry showed no EPR spectrum, suggesting that it is diamagnetic. Partial isolation of Y@C₈₂ has been achieved using high-performance liquid chromatography (HPLC) with on-line EPR detection to give an EPR-active fraction that contained C₈₄ with a trace of Y@C₈₂ (ref. 87).

The EPR spectrum of an extract containing scandium metallofullerenes (Fig. 3a) shows considerably more structure than lanthanum or yttrium spectra^{17,24}. This spectrum was modelled (Fig. 3b) by superimposing two spectra, one of which simulates h.f.c. to a single ⁴⁵Sc nucleus with spin 7/2 (Fig. 3d), and the other simulates h.f.c. to three equivalent ⁴⁵Sc nuclei (Fig. 3c). Comparison of the experimentally observed 3.82-G h.f.c. for the mono-scandium species with 60-G h.f.c. observed for Sc²⁺ in CaF₂ (ref. 88) and –120-G h.f.c. calculated for isolated Sc²⁺ (using UHF wavefunctions) suggests that the scandium in Sc@C₈₂ is also in the 3+ state. The ⁴⁵Sc h.f.c. for Sc₃@C₈₂ (6.8 G) is only slightly less than 8.5-G h.f.c. measured for

molecular Sc_3 in an argon matrix at 4.2 K (ref. 89). The extent of charge transfer to the cage is unknown in this case.

The mass spectrum of the scandium material, shown in Fig. 4, reveals that $\text{Sc}@C_{82}$ and $\text{Sc}_3@C_{82}$ are actually minor components compared with the di-scandium species $\text{Sc}_2@C_{2n}$ ($2n=80, 82, 84, 86, \dots$). The latter are EPR-silent, whereas Sc_2 isolated in a neon matrix at 4.2 K has an EPR-active quintet ground state^{90,91}. The difference in spin multiplicity between the matrix-isolated and fullerene-caged di-scandium species may indicate bonding between the fullerene cage and the trapped atoms.

Other EPR and mass spectrometric studies have shown that several different metallofullerene species with the same chemical formula are formed in a metal-graphite arc-burn^{18,21,23}. The nature of the difference between these species is still a mystery. The EPR technique has also been used to study the stability in air of the lanthanum and scandium metallofullerene isomers^{23,26,27}.

Photoelectron spectroscopy, Mössbauer spectroscopy and XAFS. Several other analytical methods have been applied to metallofullerenes. X-ray photoelectron spectroscopy (XPS) has been used to characterize solid fullerene-metallofullerene films containing $\text{La}@C_{2n}$, $\text{Y}@C_{2n}$ and $\text{Y}_2@C_{2n}$. The XPS spectra indicate that the metal atoms are protected from chemical attack and have a formal valence of 3+ (ref. 13). Similarly, XPS spectra of a film containing $\text{U}@C_{2n}$ were consistent with a formal uranium valence of 4+ (ref. 14). For $\text{Ca}@C_{60}$ entrained in a supersonic helium beam, ultraviolet photoelectron spectroscopy (UPS) carried out by Wang *et al.*^{15,16} gave an electron affinity of 3 eV (0.3 eV higher than for C_{60}). The spectra also indicated that calcium donates both valence electrons to the C_{60} cage.

Mössbauer spectroscopy is extremely sensitive to valence state for certain atoms. Pradeep *et al.*³² applied this technique to their FeC_{60} sample and concluded the iron was near zero valent, whereas Su *et al.* found that the europium in a soot containing many $\text{Eu}_m@C_{2n}$ species was trivalent⁹².

One of the few structural probes that can be applied to dilute samples of material is extended X-ray absorption fine structure (EXAFS). One EXAFS study of yttrium-metallofullerenes concluded that the Y atom is outside the cage⁹³. On the other hand, a more recent study on material containing YC_{82} and Y_2C_{82} (at 10 K and ambient temperature), indicated that the Y atoms are endohedral⁹⁴. In the latter study the data were modelled assuming 2 closest shells of 6 carbon atoms each, at 2.4 and 2.9 Å. These results are consistent with recent theoretical studies of a presumably similar species, $\text{La}@C_{82}$, which find the optimum metal-ion position to be inside the cage and ~2.5 Å from the nearest carbon atoms^{85,86}.

Theory

One would like to understand theoretically the metallofullerene formation process, their favoured cage sizes and isomers, electronic structure, chemical behaviour and solid-state properties. This is a very tall order, but a good start has been made. Early electronic structure calculations for metallofullerenes considered a rigid C_{60} cage containing a central metal atom. Rosen *et al.*^{95,96} predicted that, for $\text{La}@C_{60}$, the C_{60} levels shift down uniformly and the three metal valence electrons transfer to the cage LUMO.

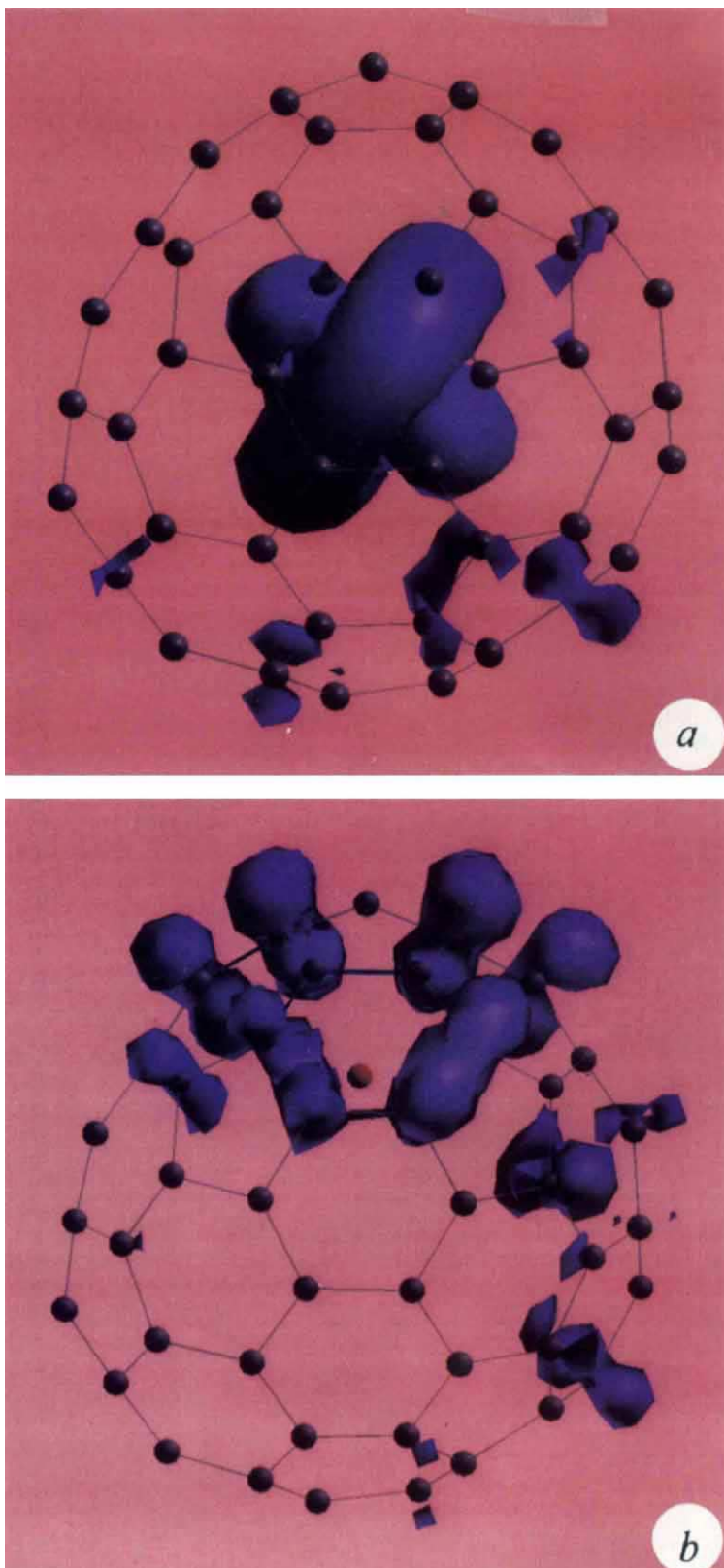


FIG. 5 Surface of constant electron density (0.01 electrons per unit of atomic volume (0.529 \AA^3)) corresponding to the HOMO state of $\text{La}@C_{82}$ with the lanthanum (red) located at the cage centre in the 2+ oxidation state (a), and at an energetically favourable asymmetric position in the 3+ state (b). The C_{82} cage (initially C_{3v} symmetry, but relaxed) is viewed perpendicular to a mirror plane. (From ref. 85, with permission.)

In contrast, a later study of this complex found a quartet ground state with only two of the lanthanum electrons transferred to the LUMO⁹⁷. Calculations with a central alkali-metal atom predicted that the metal loses its valence electron to the cage⁹⁸. Two calculations on $\text{Ca}@C_{60}$ predicted that both metal valence electrons are transferred to the cage^{99,100}, whereas a third calculation predicted a triplet ground-state complex involving monovalent calcium⁹⁷. The minimal perturbation and uniform shift of the cage molecular orbital energy levels typically found in these calculations result from the central location of the metal atom, which minimizes overlap between metal and cage orbitals and (if Jahn-Teller distortion is neglected) preserves the high cage symmetry.

Whereas endohedral rare gas atoms may be centred in C_{60} , metals may favour off-centre positions¹⁰¹⁻¹¹⁴. Motion of endohedral atoms inside fullerene cages has been analysed by a number of groups^{103-108,115,116}. Theoretical calculations are complicated by the loss of symmetry for off-centre metal positions, and by the lower-symmetry, larger cages typical of experimentally observed metallofullerenes. Nevertheless, Laasonen *et al.* recently carried out *ab initio* calculations for $\text{La}@C_{82}$ (relaxed C_{3v} cage)⁸⁵. Their results showed that the lanthanum is in a 2+ oxidation state if it is located externally, centrally, or on the 3-fold axis (see Fig. 5a). But for lower-symmetry (C_3) sites the third valence electron is lost to the cage; the resulting highest occupied molecular orbital (HOMO) is illustrated in Fig. 5b. The energy calculated for this off-centre configuration is 3.5 eV lower than for the configuration with a centrally located La. A subsequent semi-empirical calculation by Nagase *et al.* led to similar conclusions⁸⁶. Andreoni *et al.* have also carried out *ab initio* calculations for $\text{M}@C_{60}$ ($M = \text{K}, \text{Na}, \text{Al}$ and La)^{109,110}. Other recent theoretical work investigated the structures of numerous $\text{M}@C_{28}$ species¹¹⁷⁻¹²⁰, and the electronic structure of $\text{Sc}_3@C_{82}$ (ref. 121).

Why do only certain cages seem favourable for stable metallofullerene formation? In general, it is difficult to understand how fullerenes form. Some guidelines such as the 'isolated pentagon rule'^{122,123} seem to hold. Hückel molecular-orbital theory has been used by Manolopoulos and Fowler to estimate the HOMO-LUMO gaps of isolated-pentagon fullerene isomers. For normal fullerenes this approach identified successfully the preferred C_{60} , C_{70} and C_{76} cages, but was less successful for higher fullerenes¹²⁴⁻¹²⁸. By studying fullerene-dianions they identified C_{74}^{2-} , C_{82}^{2-} and C_{88}^{2-} as promising closed-shell candidates for metallofullerene formation^{129,130}. But the EPR results for $\text{La}@C_{82}$ (ref. 6) demonstrate clearly that simple 'shell closing' models^{5,129} are inadequate. (This is unfortunate because *a priori* methods are too costly for survey work.) One imaginative model for the formation of $\text{La}@C_{82}$ is based on reacting an *exohedral* $\text{La}C_{60}$ with carbon to give an endohedral complex with the metal residing in a 22-atom side cage attached to the C_{60} unit (ref. 131).

From an empirical standpoint, it is intriguing to note that in an early paper on formation of fullerenes in flames¹³², mass spectra of the negative ions showed prominent peaks for C_{2n}^- with $2n = 50, 74, 80, 82$ and 84 . All of these (except C_{50}) form stable, soluble metallofullerenes, suggesting that the electron affinity of empty fullerenes is related to metallofullerene stability, and even that the same isomers occur for both the hollow and metal-containing species. Thus an attempt to guess the cage isomer for $\text{La}@C_{82}$ (ref. 86) from NMR data on C_{82} (ref. 133) may be reasonable.

Status, directions and prospects

The idea that atoms can be trapped in fullerenes to form stable metallofullerenes has been consistently supported by spectroscopic, fragmentation and chemical evidence. The reactivity of deliberately synthesized exohedral metal-fullerene complexes compared with the relative inertness of arc-produced metallofullerenes provides particularly convincing, albeit indirect evidence

that the latter are indeed endohedral^{163,78}. An elegant experiment by Saunders *et al.*³⁵ showed the existence of minute amounts of $\text{He}@C_{2n}$ species in fullerene soot prepared using standard methods¹². Using ultra-sensitive mass spectrometry they found that at temperatures of $\sim 800^\circ\text{C}$, the fullerenes released ^4He and ^3He in the ratio expected for tank helium rather than atmospheric helium, proving that the gas was trapped in the fullerenes during formation in the presence of the tank helium. Similar results were obtained with neon³⁵. The unprecedented observation of stable inert-gas-carbon complexes can only be explained if the inert-gas atoms are encapsulated. Thus, despite the lack of direct structural data, the accumulated evidence leaves little doubt that endohedral fullerenes exist.

Application of most traditional spectroscopic techniques and structural techniques (X-ray, electron or neutron diffraction) to endohedral fullerenes has been impeded by the difficulty in producing pure samples. The technique of EPR spectroscopy, which selectively detects radical metallofullerenes, has provided the most detailed electronic structural information to date, particularly the oxidation state of the metal atom and the spin multiplicity of the complexes. Important progress toward purification of metallofullerenes has recently been reported by two groups using multiple HPLC stages to obtain pure samples of $\text{Sc}_2@C_{2n}$, with $2n = 74, 82$ and 84 (refs 27, 29), and pure $\text{La}@C_{82}$ (see Fig. 5)²⁸. As a result of these purification efforts the first ultraviolet, visible^{28,29} and infrared²⁸ spectra of these materials have been obtained, and scanning tunnelling microscopy (STM) images of metallofullerenes on a surface have been made¹³⁴. The STM images, taken of $\text{Sc}@C_{74}$ and $\text{Sc}_2@C_{74}$ on a silicon surface, show the molecules to be spherical with apparent cage diameters

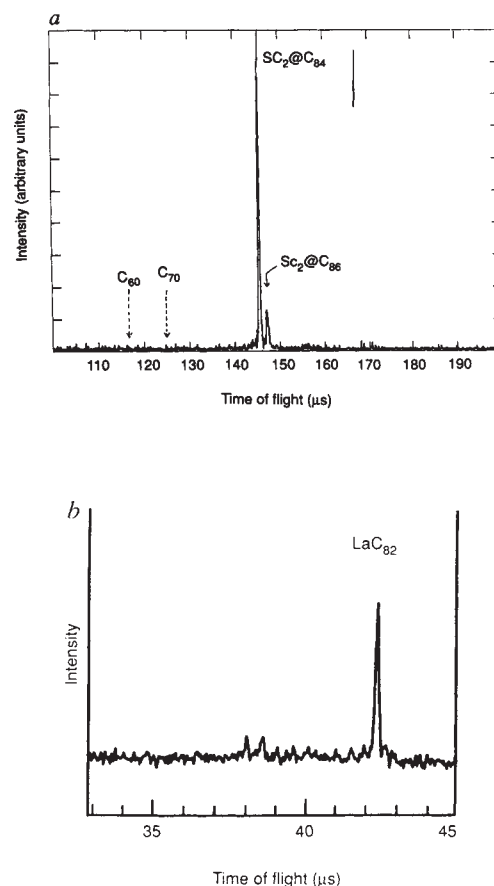


FIG. 6 Mass spectra of the first purified metallofullerene species. a, $\text{Sc}_2@C_{84}$ (from ref. 29, with permission); b, $\text{La}@C_{82}$ (from ref. 28, with permission).

of $\sim 9.5 \text{ \AA}$. Exploration of the properties of these novel materials should accelerate in light of these developments.

Important questions remain as spurs for further research. Can alternative routes to bulk production of endohedral species be developed, perhaps using cage-opening reactions or direct rational synthesis? Which species can be encapsulated? Can large quantities of purified endohedral fullerenes be efficiently made?

Above all, what are their various physical properties? Beyond their scientific interest, the possibility of developing important applications for endohedral fullerenes will hinge on the answers to such questions. □

D. S. Bethune, R. D. Johnson, J. R. Salem, M. S. de Vries and C. S. Yannoni are at IBM Research Division, Almaden Research Center, 650 Harry Road, San Jose, California 95120-6099, USA.

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